Response to Referee#2

Dear Referee,

Thanks for giving us an opportunity to revise our manuscript (acp-2022-752). We appreciate your constructive comments and suggestions. We have studied them carefully and made revisions on the manuscript. These comments, suggestions and the corresponding replies are listed below.

Note that the title has been changed to "Impact of aerosol optics on vertical distribution of ozone in autumn over YRD" to clarify the study region and applicability.

The referee's comments are highlighted by gray. Followed by the comments are our responses. The texts led by **line number** are the current texts in manuscript, with some important revisions colored by red.

With regards,

Shuqi Yan, Bin Zhu*, and all co-authors.

General comments:

More discussions are needed to clarify the meaning and limitations of this research. This is important for other researchers to consider the applicability of this study. Observations from the field campaign can be included to support the results concluded from model simulations. In addition, I suggest modifying the titles of section 3.2, 3.3 and 3.4 to convey the main topic of each section more clearly.

Thanks for this suggestion. We have addressed this comment by the following aspects:

1) Limitations of this research

The original simulation period is rather short (just several days). We have extended the simulation period to be one month (15 Oct to 15 Nov). We evaluate the model performance in the whole month, revealing that the model can reasonably capture the variation of temperature, wind, $PM_{2.5}$ and ozone (Section 3.1). We compare the aerosol effect on ozone under different pollution conditions, finding that aerosols cause more ozone reduction in polluted conditions than in clean conditions (Section 4).

This study is only applicable to autumn season. In spring and summer, the weather systems over Yangtze River Delta Region vary significantly and precipitation events frequently occur. In winter, the solar radiation is relatively weak, so the ozone concentration is commonly not high. Therefore, we conduct our field observations mostly in autumn season.

The WRF-Chem model has limitations in describing aerosol mixing state, which has been stated in the current manuscript (Section 2.3).

In Section 2.3

(The definitions of mixing states and model experiments.....). One should note that the real-world aerosol mixing state varies with emission, meteorology, composition, and other factors. The dynamic evolution of aerosol mixing state and its influencing factors have not been addressed in most current 3D models (Matsui et al., 2013). This work addresses aerosol optics by the three ideal mixing states, which will inevitably cause the simulated aerosol optics deviating from observation.

In Section 3.1

Four Additional sites around Nanjing, i.e., Changzhou (CZ), Huainan (HN), Maanshan (MS), and Huaian (HA) (Figure 1) are chosen to evaluate the performance on the time variation of meteorological parameters (temperature, wind speed and wind direction), $PM_{2.5}$ and ozone in the base experiment (internal mixing). The statistical metrics include index of agreement (IOA),

mean bias (MB), root mean square error (RMSE), mean normalized bias (MNB) and mean fractional bias (MFB). The calculations are from Lu et al. (1997), especially, the IOA of wind direction is from Kwok et al. (2010). Benchmark values of meteorology and air pollutants are derived from Emery et al. (2011) and EPA (2005; 2007). The temporal variations of simulated meteorology and air pollutants are generally in good agreement with observations (Figure 2). From Table 3, temperature presents the highest IOA, with a slightly large MB at HA site. The simulated wind direction is similar to observation, and MB exceeds benchmark value at only one site. The simulated wind speed is a bit higher, which is because the WRF model tends to overestimate wind speed due to the description of surface roughness (Jia and Zhang, 2020, 2021; Jiménez and Dudhia, 2012). $PM_{2.5}$ is moderately overestimated, but all the metrics are within the benchmarks. The IOA of ozone exceeds 0.8 at all sites, and only one site shows a MNB out of benchmark. The model statistical metrics of $PM_{2.5}$ and ozone are consistent with previous works (Chen et al., 2022; Hu et al., 2016; Singh et al., 2012; Zhang et al., 2014a). Generally, the base experiment simulations on the temporal variation of meteorology and air pollutants are acceptable, which reasonably reproduces the observations in the atmosphere.

Table 3. The statistic metrics of the model performance on time series of temperature (Tem), wind speed (WS), wind direction (WD), $PM_{2.5}$ and ozone. The benchmark values are from Emery et al. (2011) and EPA (2005; 2007). Metrics that out of bechmarks are marked with red.

Variable	Metric	NJ	CZ	HN	MS	HA	benchmark
Tem	IOA	0.97	0.97	0.96	0.97	0.96	>0.8
	MB	0.18	0.18	0.42	0.31	0.50	<±0.5
	RMSE	1.07	1.07	1.43	1.10	1.52	
WS	IOA	0.64	0.63	0.66	0.71	0.64	>0.6
	MB	0.47	0.68	0.52	-0.05	0.71	<±0.5
	RMSE	1.13	1.06	1.09	0.88	1.09	<2
WD	IOA	0.94	0.93	0.93	0.95	0.88	
	MB	-3.32	10.47	9.91	-4.65	6.16	<±10
	RMSE	35.91	38.53	46.31	36.56	52.92	
$PM_{2.5}$	IOA	0.74	0.84	0.83	0.64	0.86	
	MNB	0.26	0.01	0.12	0.36	0.34	
	MFB	0.17	-0.04	0.06	0.23	0.22	<±0.6
Ozone	IOA	0.87	0.88	0.91	0.83	0.88	
	MNB	-0.07	-0.03	0.03	0.03	0.20	<±0.15
	MFB	-0.15	-0.07	0.02	0.03	0.17	

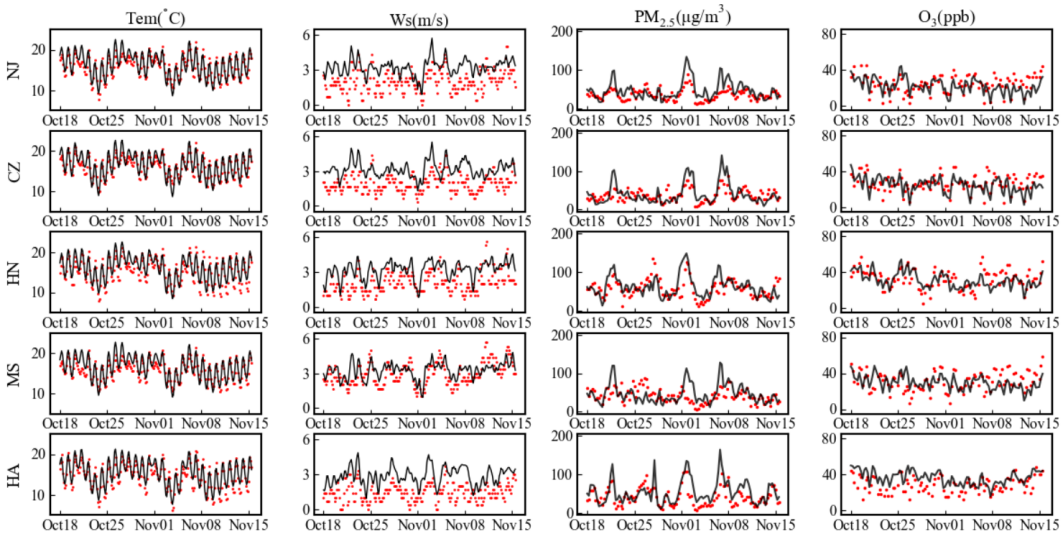

Figure 2. Model evaluations on the time series on temperature (Tem), wind speed (Ws), $PM_{2.5}$ and Ozone at five sites. The Changzhou (CZ), Huainan (HN), Maanshan (MS) and Huaian (HA) sites are located to the east, west, south and north of Nanjing, respectively. The red dots are observations and black lines are simulations (after 3-point running average). The time range is from 08:00 on 15 October to 20:00 on 15 November.

In Section 4

The ozone variations during representative clean and polluted episodes are shown in Table 5. The ozone concentrations within BL in internal mixing experiment are consistently reduced during all episodes. The core-shell mix-

ing state shows slightly lower reductions than internal mixing, and the ozone reductions are the least in external mixing state. The differences in ozone relative changes between clean and polluted episodes are distinct. For example, in the internal mixing state, the relative reductions are about 0~5% in clean episodes and 6~11% in polluted episodes, indicating that the aerosol effect is more profound under high aerosol contents. On 2 November which is the highest pollution episode during the study period, the relative changes of ozone are approximately -11~-2%. It can be inferred that aerosol effect on photolysis rates, ozone precursors and ozone concentration might be consistent under different underlying surface and pollution conditions, and it is more significant in polluted conditions.

Table 5. The diurnal averaged (08:00~17:00) quantities within BL during some representative clean and polluted episodes. The PM2.5 (μg/m3) and ozone (ppb) are the values in the base experiment (internal mixing). The last three columns are the changes and relative changes of ozone under different mixing states.

Date	$PM_{2.5}$	Ozone	Δint	Δcsm	Δext
Clean episode					
10-19	32	53	-1.9 (-3.5%)	-1.7 (-3.1%)	+0.0 (+0.0%)
10-20	18	49	-0.8 (-1.5%)	-0.7 (-1.4%)	+0.1 (+0.1%)
10-25	28	53	-2.0 (-3.6%)	-1.9 (-3.5%)	-0.2 (-0.3%)
11-03	33	39	-0.7 (-1.8%)	-0.7 (-1.8%)	-0.4 (-1.1%)
11-05	17	44	-1.5 (-3.3%)	-1.5 (-3.3%)	-0.9 (-1.9%)
11-12	23	36	-1.9 (-4.9%)	-1.9 (-4.9%)	-0.9 (-2.5%)
Polluted episode					
10-22	91	46	-3.0 (-6.1%)	-2.8 (-5.6%)	-0.3 (-0.7%)
11-02	111	56	-7.7 (-10.5%)	-6.4 (-8.6%)	-1.5 (-2.0%)
11-07	87	39	-4.6 (-10.7%)	-4.6 (-10.6%)	-1.6 (-3.7%)
11-08	82	39	-3.0 (-7.0%)	-2.8 (-6.6%)	-0.6 (-1.4%)

2)Can observations from the field campaign support the results of model simulations?

A prior work by Shi et al. (2022) studies the effect of aerosols on photolysis and ozone profiles by observations from field campaign. It is found that aerosols inhibit ozone production in the lower BL and enhance photolysis and ozone production at upper BL. The observation data in this work is the subset of Shi et al. (2022).

References

Shi, S., Zhu, B., Tang, G., Liu, C., An, J., Liu, D., Xu, J., Xu, H., Liao, H., & Zhang, Y.: Observational evidence of aerosol radiation modifying photochemical ozone profiles in the lower troposphere, Geophys. Res. Lett., 49, e2022GL099274, https://doi.org/10.1029/2022GL099274, 2022.

3)The titles of Section 3.2~3.4 should be modified.

It has been modified to convey the exact meanings:

Section 3.2: ~~Impact of aerosol-BL interactions~~ Impact of aerosols on BL and NO_X

Section 3.3: ~~Impact of aerosol-photolysis interactions~~ Impact of aerosols on photolysis

Section 3.4: ~~Impact of aerosol-BL and aerosol-photolysis interactions~~ Impact of aerosols on ozone profile

Specific comments:

S1. Line 76-78: "We mainly use the data from 2 to 5 November to study the effect of aerosols on ozone, and detailly investigate the physical and chemical mechanisms in the pollution stage on 2 November". I can not find related results in the manuscript.

In the current version, the simulation period has been extended from just a few days (2 to 5 November) to a month (15 October to 15 November). We have clearly stated when to use the whole simulation period and

when to use the single day of 2 November (in the leading text of Section 3).

In Section 3

It is an obvious pollution stage on 2 November 2020. The model evaluation on profiles (Section 3.1) and the mechanism of aerosols affecting ozone variation at the Nanjing site (Sections 3.2 to 3.4) are presented during that day. The model evaluation on time series (Section 3.1) and the aerosol effect under different pollution conditions (Section 4) are presented during the simulation period (15 October to 15 November).

S2. Line 88: Which year's emission inventory was used in this study?

The original year is 2016. In the current version, we have acquired new inventories from MEIC Group, so the base year is changed to be 2020, the exact year of the simulation period.

S3. Section 3.2: I'm confused about the content in this section. Why did you just describe the changes of NOx affected by aerosol-BL interactions instead of Ozone and PM2.5.

Thanks for this suggestion. We agree that the section titles did not convey the exact meanings. The section titles have been changed.

Section 3.2: ~~Impact of aerosol-BL interactions~~ Impact of aerosols on BL and NO_X

Section 3.3: ~~Impact of aerosol-photolysis interactions~~ Impact of aerosols on photolysis

Section 3.4: ~~I~~~~mpact of aerosol-BL and aerosol-photolysis interactions~~ Impact of aerosols on ozone profile

S4. Line 161-162: Does ozone here mean that in BL?

Yes. Our original focus is ozone within BL. We have stated it more clearly.

In Section 3.4

Figure 7 shows the ozone profile in various mixing states. We focus on the ozone within BL in the daytime. During 08:00~11:00, ……(the descriptions of BL ozone).

S5. Line 163: Should be "a strong positive gradient".

Thanks for this suggestion. This typo has been corrected.

S6. Section 3.4: Discussions about the differences between three aerosol mixing states in process analysis are rare, I suggest adding some content to explain the differences described in the first paragraph.

Thanks for this suggestion. We have added more discussions about ozone vertical variation, and removed some contents about the differences between three aerosol mixing states in process analysis.

In Section 3.4

Figure 7 shows the ozone profile in various mixing states. We focus on the ozone within BL in the daytime. During 08:00~11:00, the BL is in increasing stage, and ozone increases with height within BL. The average changes in ozone under internal, core-shell and external mixing are -9.7ppb (-15.8%), -8.5ppb (-13.8%) and -3.3ppb (-5.4%), respectively. As BL develops during 11:00~17:00, ozone shows a strong positive gradient near the surface, uniform distribution above the surface and negative gradient at upper BL. The average change in ozone under internal, core-shell and external mixing is -7.3ppb (-9.3%), -5.9ppb (-7.5%) and -1.0ppb (-1.2%), respectively. During the daytime (08:00~17:00), ozone reduction is larger in internal (10.5%) and core-shell mixing states (8.6%) and the smallest in external mixing state (2.0%). The reduction (about 3~13%) is the largest at near surface, which is due to that the NO_X accumulation and photolysis inhibition are more profound at near surface. Other studies also reveal that ozone reductions caused by aerosols are approximately in the range of 10~20% (e.g., Gao et al., 2020; Qu et al., 2021; Yang et al., 2022). Above surface where the layer is more well-mixed, ozone reduction is relatively weaker. It can be inferred that diurnal ozone concentration is generally reduced in all mixing states and at all heights within BL. The reduction is the smallest in external mixing state. It could be because the enhanced NO titration effect associated with NOx accumulation is weaker in external mixing than in other mixing states

(Figure 4c). Also, externally mixed aerosols lead to less photolysis suppression in the lower level and larger photolysis enhancement in the upper level (Figure 6a and b), which will partly counteract the reduction in ozone concentration

In Section 3.4

~~Table 4 quantitatively describes the respective contributions of three processes to ozone variation during 11:00~17:00. From near surface to lower BL (0~300m), the positive VMIX contribution is stronger than the negative CHEM contribution, and the role of ADVC can be ignored. At lower to middle BL (300~800m), the promoting effect of VMIX on ozone weakens, and instead, the negative contribution of CHEM turns to positive and becomes the dominant influencing factor. At the upper BL (800~1500m), VMIX plays the dominant role due to the increasing ozone entrainment at upper BL (Figure 8b-d). The relative contributions of the three processes are generally consistent in all mixing states.~~

	~~int~~	~~esm~~	~~ext~~
~~H: 0~300m~~			
~~Δvmix~~	~~+2.9 (+53.2%)~~	~~+2.8 (+53.7%)~~	~~+2.3 (+57.4%)~~
~~Δchem~~	~~-2.2 (-39.5%)~~	~~-2.0 (-38.7%)~~	~~-1.5 (-37.3%)~~
~~Δadvc~~	~~+0.4 (+7.4%)~~	~~+0.4 (+7.5%)~~	~~+0.2 (+5.4%)~~
~~H: 300~800m~~			
~~Δvmix~~	~~+0.0 (+3.0%)~~	~~-0.2 (+13.2%)~~	~~-0.4 (-25.1%)~~
~~Δchem~~	~~+0.5 (+52.6%)~~	~~+0.5 (+57.6%)~~	~~+0.8 (+65.8%)~~
~~Δadvc~~	~~+0.4 (+44.4%)~~	~~+0.4 (+29.1%)~~	~~+0.2 (+9.2%)~~
~~H: 800~1500m~~			
~~Δvmix~~	~~-1.5 (+71.9%)~~	~~+2.0 (+79.0%)~~	~~+1.4 (+65.5%)~~
~~Δchem~~	~~+0.1 (+3.1%)~~	~~-0.0 (-0.3%)~~	~~+0.6 (+28.2%)~~
~~Δadvc~~	~~+0.5 (+25.1%)~~	~~+0.5 (+20.7%)~~	~~+0.1 (+6.3%)~~